Calculated Effects of Ga on the Pu Lattice after the δ to α Transformation

Sven P. Rudin and John M. Wills, T-1

The doping of plutonium with gallium atoms stabilizes the technologically important delta structure (face-centered cubic crystal structure) down to room temperature. As the temperature is lowered further, the delta structure transforms into the α-Pu structure with the Ga atoms arranged randomly on the eight symmetrically inequivalent alpha sites. This so-called α′ structure has an expanded volume relative to the (undoped) α-Pu lattice, but with thermal treatment the volume expansion decreases [1].

To further the understanding of these thermal effects we have performed density functional theory (DFT) calculations to investigate the local effects of substitutional Ga doping on the α-Pu structure. In a first step the lattice was held fixed and the total energies compared. A clear correlation emerges between the proximity of Pu atoms around each of the eight sites (Fig. 1) and the energy of the crystal where that site's Pu atom has been replaced by Ga (Fig. 2): the more distant the neighbors, the lower the energy.

This preference for having the Pu atoms farther away from the substitutional Ga atom appears to agree with experiment. Assuming the crystal's volume expands to give the Ga atom the preferred larger distance to its neighbors, the Ga atom will cause a different amount of volume expansion depending on which site it occupies. With thermal treatment the Ga atoms diffuse to energetically more favored sites which allows the volume to reduce its expansion. Further evidence for this appears in the next set of calculations where the lattice positions are allowed to relax (with the volume fixed at the α-Pu equilibrium

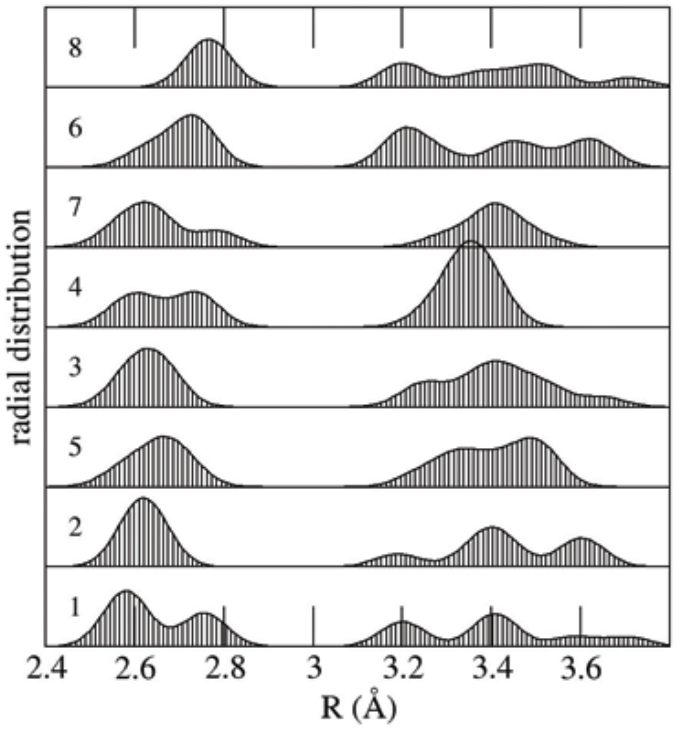

Fig. 1.
Radial distributions of Pu atoms surrounding each of the eight symmetrically unique lattice positions in the α-Pu structure. The distributions are plotted from bottom to top with increasing distance to the nearest neighbors. Each neighbor's position is smeared with a Gaussian for visualization.

volume): the distances between Ga atom and neighboring Pu atoms increases as shown in Fig. 3.

When the volume is allowed to relax in the calculations, the qualitative agreement with experiment remains. The relaxed volume is somewhat smaller than the experimental value for both pure and Ga-doped α-Pu due to the approximation inherent in DFT calculations. Still, the Ga-doped crystal remains expanded relative to pure α-Pu, and the energy remains lower for crystals whose substitutional Ga atoms have the most distant Pu neighbors.

For more information contact Sven Rudin at srudin@lanl.gov.

[1] S. S. Hecker, et al., *Prog. Mat. Sci.* **49**, 429 (2004).

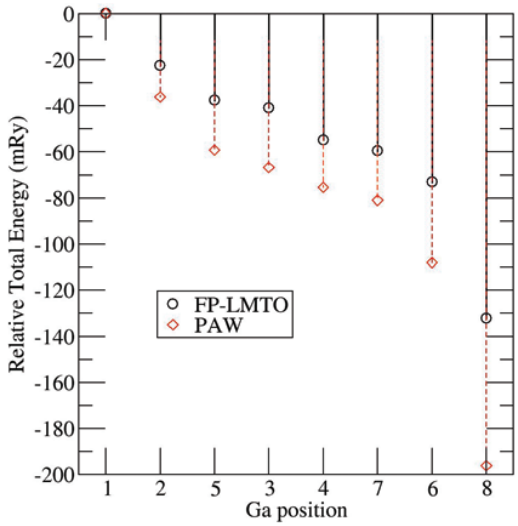

Fig. 2.
Relative energies calculated by substituting Ga for Pu on one of the eight symmetrically unique lattice positions in the α-Pu structure. The energies are relative to the energy of the 16-atom cell with the Pu atom at site 1 substituted by a Ga atom. The main difference between the two FP-LMTO and PAW calculations is the inclusion and exclusion of spin-orbit coupling, respectively.

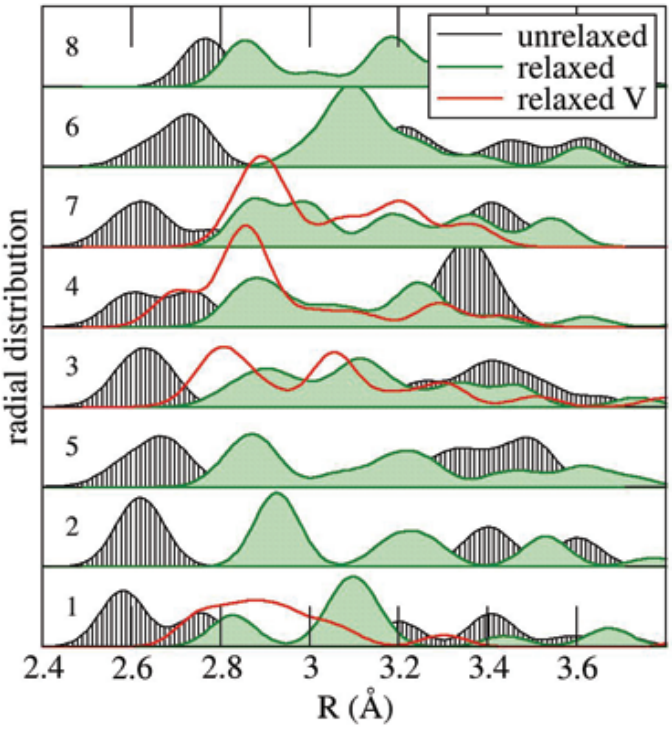

Fig. 3.
Radial distribution of Pu atoms surrounding each of the eight symmetrically unique lattice positions in the unrelaxed α-Pu lattice as well as after Ga substitution and lattice relaxation at fixed volume ("relaxed") and with relaxed volume ("relaxed V"). Relative to the unrelaxed α-Pu lattice, the substitutional Ga atom pushes its neighbors away.